UDK 669.3:620.17
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 45(5)463(2011)

OPTICAL PROPERTIES OF PLASTICALLY DEFORMED COPPER: AN ELLIPSOMETRIC STUDY

OPTIČNE LASTNOSTI PLASTIČNO DERFORMIRANEGA BAKRA: ŠTUDIJ ELIPSOMETRIJE

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Prejem rokopisa – received: 2011-01-15; sprejem za objavo – accepted for publication: 2011-03-18

In this paper the results of optical properties investigations on plastically deformed copper are presented. The optical properties of the plastically deformed copper were studied using spectroscopic ellipsometry in the ultraviolet-visible (UV-VIS) range. Chemically pure copper was deformed by applying the Equal Channel Angular Pressing (ECAP) technique. During the last decade, equal-channel angular pressing procedure was used for the fabrication of ultrafine-grained metals and alloys. The plastic deformation of metallic materials leads to the production of bulk nano-scale structures with ultrafine grains and cross-sections, which remain about equal before and after deformation. The parameters of the sample were calculated using a two-film model together with the Bruggeman effective medium approximation.

Key words: ellipsometric spectroscopy, atomic force microscopy, copper, amorphisation

V članku so predstavljeni rezultati raziskav optičnih lastnosti plastično deformiranega bakra. Te so bile raziskane s spektralno elipsometrijo v območju vidne UV-svetlobe. Kemijsko čist baker je bil deformiran z uporabo ECAP-metode (enakokotno koničasto stiskanje). V zadnjem času se ECAP-postopek uporablja za izdelavo ultra udrobnjenih kovin in zlitin. Takšna plastična deformacija kovinskih materialov vodi k izdelavi masivnih nanostruktur z ultra drobnimi zrni in prečnim prerezom, kar omogoča približno enakost pred deformacijo in po njej. Parametri preiskanih vzorcev so bili izračunani na osnovi uporabe dvojne plasti – filma skupaj s Bruggemanovo srednjo efektivno aproksimacijo.

Ključne besede: elipsometrična spektroskopija, atomska mikroskopija, baker, amorfizacija

1 INTRODUCTION

Modern life has a number of applications for copper, ranging from coins to pigments, and demand for copper remains high, especially in industrialized nations. Many consumers interact with copper in various forms on a daily basis. Copper is used in a vast variety of products in the domestic and industrial domains as thermal and electrical conductors and as a constituent of various metal alloys, in building construction, power generation and transmission, manufacturing of electronic products, and the production of industrial machinery and transportation vehicles.[1] Copper wiring and plumbing are integral to appliances, heating and cooling systems, and telecommunications links used every day in homes and businesses.

Copper is easily worked, being both ductile and malleable. It is easily stretched, molded, and shaped; it is resistant to corrosion; and conducts heat and electricity efficiently. As a result, copper was important to early humans and continues to be a material of choice for a variety of domestic, industrial, and high-technology applications today.

The most important use of copper is in electrical wiring; it is an excellent conductor of electricity (second only to silver), it can be made extremely pure, it corrodes very slowly, and it can be formed easily into thin wires – it is also very ductile. Due to this property, copper has been widely used as an electrode in electrochemical studies.[2]

Copper can be machined, although it is usually necessary to use an alloy for intricate parts, such as threaded components, to get really good mach inability characteristics. Good thermal conduction makes it useful for heat sinks and in heat exchangers. It has excellent brazing and soldering properties and can also be welded, although the best results are obtained with gas metal arc welding.[3]

Copper has a reddish, orange, or brownish color because a thin layer of tarnish (including oxides) gradually forms on its surface when gases (especially oxygen) in the air react with it. But pure copper, when fresh, is actually a pinkish or peachy metal. Copper, cesium and gold are the only three elemental metals with a natural color other than gray or silver.[4] Copper has its characteristic color because of its unique band structure.

The aim of this paper is to examine the gradient in the microstructure and texture that develops during Equal Channel Angular Pressing (ECAP).

2 EXPERIMENTAL

A chemically pure copper sample (99.99), prepared as a specimen of square cross-sections (10 mm ×10 mm) and about 50 mm long, was extremely plastically deformed with the repeated application of the Equal Channel Angular Pressing (ECAP).[5] ECAP is a novel technique for producing an ultra-fine-grain structure at the submicron level by introducing a large amount of shear strain into the material without changing the built shape or dimensions.

The deformations were performed in our experimental hydraulic press (VEB WEMA 250 MP), equipped with a tool for ECAP. The tool consists of two intersecting channels with the same cross-section (10 mm × 10 mm) that meet at an angle $2\Phi = 90°$. The geometry of the tool ensures that the material is deformed by a simple shear in ideal, frictionless conditions. The cross-section of the specimen remains almost equal before and after each step of the process, thus it is possible to subject one specimen several times to ECAP in order to reach a high degree of plastic deformation. In our case, the sample of chemically pure copper was subjected to the ECAP process eight times at room temperature (20 °C).

An atomic force microscope (AFM) was used to determine the general cell wall structure together with the assembly of particular components into the wall structure as a whole.

Ellipsometric measurements were a versatile and powerful optical technique for the investigation of the dielectric properties, used to characterize surface changes, optical constants of bulk or layered materials, overlayer thicknesses, multilayer structures, and surface or interface roughness.[6] The variable-angle spectroscopic ellipsometer (VASE) SOPRA GES5–IR in the rotating polarizer configuration was used for the ellipsometric measurements. The data were collected over the range from 1.5 eV to 4.2 eV with a step of 0.05 eV for three different angles of incidence 65°, 70° and 75°. The 70° angle was chosen as the apparatus has the maximum sensitivity for the ellipsometric data. All the calculations were made using Winelli_II Version 2.0.0.0. The fitting of the model to the experimental data was done using the Levenberg-Marquardt algorithm.[6–7]

3 RESULTS AND DISCUSSION

During our research, two copper samples were deformed and analyzed: Cu 1 – cross-section surface and Cu 2 – longitudinal section surface.

The typical appearance of the initial, undeformed Cu sample is present in **Figure 1a**. The topological morphology in two directions, longitudinal and transverse, is shown in **Figures 1b** and **1c**. As one can see from the figures, on the longitudinal surface there are essentially less phases than on the transverse surface. These phases (particles contour) probably corresponds to nano-sized crystalline phases.

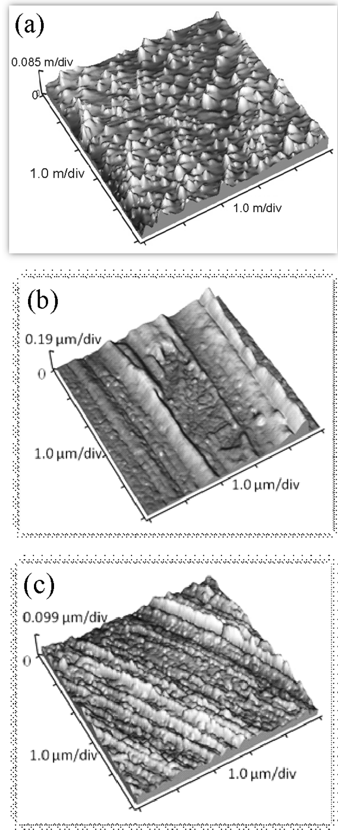

Figure 1: AFM image of surface of the pure Cu (a), Cu 2 (b) and Cu 1 (c) samples
Slika 1: AFM-slika površine čistega Cu (a), Cu 2 (b) in Cu 1 vzorcev

Ellipsometry is an optical measurement technique that characterizes light reflection (or transmission) from samples.[8] The key feature of ellipsometry is that it measures the change in polarized light upon light reflection from a sample (or light transmission by a sample). The ellipsometry measures the two values: the amplitude ratio ψ and phase difference Δ between the light waves. These parameters are defined by:

$$\rho = r_p / r_s = \tan(\psi)\, e^{i\Delta} \quad (1)$$

where ρ is the complex reflectance ratio, r_p and r_s are the complex reflectance coefficients of light polarized parallel (p) and perpendicular (s) to the plane of incidence, respectively.

The ellipsometric quantities ψ and Δ are sensitive to changes of different parameters, such as surface conditions, over layer structure, dielectric function of the material and others.

The real and imaginary parts of the pseudo-dielectric function for the bulk copper and samples Cu 1 and Cu 2 are presented in **Figure 2**. When it is exposed to oxygen, copper naturally oxidizes to copper(I) oxide (Cu_2O), therefore the ellipsometric spectra ($\tan(\psi)$, $\cos(\Delta)$) of the two samples Cu 1 and Cu 2 were fitted using a two-film

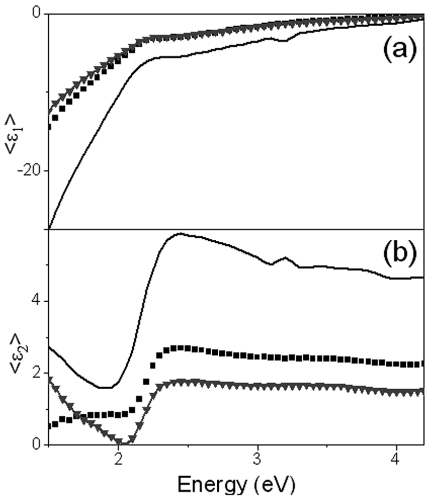

Figure 2: Real (a) and imaginary (b) parts of the pseudo–dielectric function for Cu 1 (squares), Cu 2 (triangles) and bulk copper (solid line)

Slika 2: Realni (a) in imaginarni (b) del pseudo-dialekrične funkcije za Cu 1 (kvadrat), Cu 2 (trikotnik) in masivni baker (polna črta)

model: Cu as a substrate, an over layer of Cu_2O and a surface-roughness layer (**Figure 3a**). The influence of the surface roughness also has to be taken into account. Namely, the surface over layer roughness is composed of the bulk copper oxide and an ambient. We calculated the volume fraction of the constituents. [6]

The experimental and the best-fitting data of the sample Cu 1 are presented in **Figure 3b**. The experimental data are represented by circles, while the solid lines represent the fitted data. The thickness of the Cu_2O

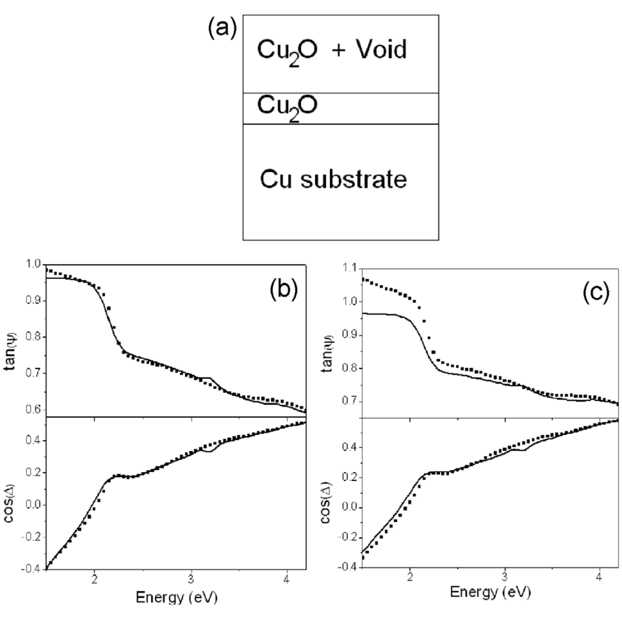

Figure 3: Sketch of a two-film model (a), experimental data (dots) and fitted data (solid line) of the ellipsometric spectra of samples Cu 1 (b) and Cu 2 (c)

Slika 3: Skica dvoplastnega modela: (a) eksperimentalni podatki (pikice) in dobljeni podatki (polna črta) elipsoidnega spektra za vzorca Cu 1 (b) in Cu 2 (c)

was about 1.5 nm, and the roughness of the over layer with 80 % of Cu_2O and 20 % of void was about 25.6 nm. For the energies above 2 eV this fit is better than for the energies around and below this value. This is a consequence of plastic deformation, because the dielectric function of the sample substrate differs from the one of the bulk copper.[9]

The experimental and the best-fitting data of the sample Cu 2 are presented in **Figure 3c**. The thickness of the copper oxide was about 1.7 nm, and the roughness over layer, with 81 % of oxide and 19 % of voids, was about 35 nm. Comparing these two fits, it is obvious that the model with Cu_2O and surface roughness is more appropriate for the case of the Cu 1 sample, than for the case of the Cu 2 sample.

4 CONCLUSION

Ellipsometric measurements were used to determine the optical properties of plastically deformed copper. The thickness of the spontaneously formed copper oxide and the surface roughness was calculated by applying a two-layer model. We showed that this model is better suited for the microstructure investigation of the sample Cu 1 – cross-section surface than for the Cu 2 – longitudinal section surface. The obtained results indicated that the plastic deformation of the sample did not lead to total amorphization of the specimen.

ACKNOWLEDGMENTS

This work is supported under the Programme of Scientific and Technological Cooperation between the Republic of Slovenia and the Republic of Serbia. The work in Serbia is supported by the Serbian Ministry of Science and Technological Development (Project III 45003). This paper is part of the Slovenian MNT ERA-NET Project No. 3211-07-000023: Nano Structured Metal Ceramic Composites.

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